

# Preparation and thermoelectric properties of some phosphide skutterudite compounds

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## Abstract

Thermoelectric properties of  $\text{CoP}_3$  and  $\text{CeFe}_4\text{P}_{12}$  have been measured for the first time. These compounds were synthesized by a flux technique using Sn as the solvent. The samples were characterized by x-ray diffractometry and electron microprobe analyses. The Seebeck coefficient, the electrical resistivity, the Hall effect, and the thermal conductivity were measured over a wide range of temperature. The results indicate that  $\text{CoP}_3$  and  $\text{CeFe}_4\text{P}_{12}$  are semiconductors, in agreement with theoretical predictions. The thermal conductivity of  $\text{CeFe}_4\text{P}_{12}$  is about ten times larger than for  $\text{CeFe}_4\text{Sb}_{12}$  which is primarily due to both a reduced motion of the Ce ions in smaller voids and lower hole-phonon scattering. The results are analyzed and discussed to provide guidelines for optimization of the thermoelectric properties of these materials.

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## I. INTRODUCTION

Much interest has been devoted over the last several years to the study of the thermal and electrical properties of a class of materials called skutterudites. Since they were first identified as potential thermoelectric materials, a number of these compounds have been studied both theoretically and experimentally. To be a useful thermoelectric, the materials must have a large thermoelectric figure of merit, defined as  $ZT = \alpha^2 T / \rho \lambda$ , where  $\alpha$  is the Seebeck coefficient,  $\rho$  the electrical resistivity, and  $\lambda$  the thermal conductivity. Large  $ZT$  values have been achieved for some skutterudite compounds at high temperatures<sup>1,2</sup>. A large number of these compounds exist, offering numerous possibilities for optimizing their thermoelectric properties in different temperature ranges.

Skutterudite type compounds are cubic and belong to the  $Im\bar{3}$  space group. A number of materials having this structure have been identified<sup>3-12</sup>. Skutterudite compounds can be divided into two main groups, filled and unfilled. Binary unfilled compounds have the general formula,  $\text{AX}_3$ , where  $\text{A} = \text{Co}, \text{Rh}, \text{Ir}$  and  $\text{X} = \text{P}, \text{As}, \text{Sb}$ . There are two voids in the unit cell of these compounds. While these unfilled materials possess high hole mobility and large Seebeck coefficient, they also tend to have relatively large thermal conductivity (especially around room temperature) which is obviously not favorable for achieving high  $ZT$  values. The filled compounds, where the voids are partially or completely filled with rare-earth or alkaline earth atoms (R), have the general formula,  $\text{RM}_4\text{X}_{12}$ , where M is a transition metal. In these materials, much lower thermal conductivity have been obtained compared to those measured on binary compounds. The decrease in thermal conductivity for filled compounds is primarily attributed to the loosely bound atoms in the cages which "rattle" in the large cages and perturb the phonon transport, as originally predicted by Slack and Tsoukala<sup>13</sup>.

These findings have generated a number of studies of the electronic, magnetic, and thermal properties of these compounds. Most experimental studies have been conducted on Sb-based filled and unfilled skutterudite compounds<sup>1,2,11-21</sup>. Most Sb-based filled compounds show metallic-type behavior and the optimization of their thermoelectric properties, i.e. doping, is therefore somewhat difficult. Although some P-based filled and unfilled compounds have been synthesized, very limited data is available on their thermoelectric properties. Theoretical and experimental studies have shown that some of these compounds are semiconductors<sup>22-28</sup> and their thermoelectric properties might therefore be easier to optimize. As the first step in investigating the potential of P-based skutterudite compounds, we have synthesized and measured the thermoelectric properties of  $\text{CoP}_3$  and  $\text{CeFe}_4\text{P}_{12}$  which are predicted to be semiconductors with band gap<sup>22</sup> of 0.28 and 0.34 eV<sup>23</sup>, respectively. The thermal and electrical properties are discussed and compared to their Sb-based analogs.

## II. EXPERIMENTAL DETAILS

Single phase crystals of  $\text{CoP}_3$  and  $\text{CeFe}_4\text{P}_{12}$  were synthesized by a flux technique using Sn as the solvent. Co powder (99.998% pure), cerium powder (99.9% pure), iron sponge (99.6% pure), phosphorus pieces (99.995% pure), and tin granules (99.5% pure) were used and loaded into fused quartz tubes (20 mm in diameter and 20 cm long) which were evacuated to  $10^{-5}$  Torr and sealed. The ratio of starting materials were  $\text{Co:P:Sn} = 1:3:25$  and  $\text{Ce:Fe:P:Sn}^8 = 1:4:20:50$ . The former mixture was heated at 50 C/h to 780 C, soaked for 1 week and cooled at 2 C/h to room temperature. The latter was heated at 50 C/h to 777 C, soaked for 1 week, cooled at 2 C/h to 460 C and then left in the furnace to cool down to room temperature. HCl was used to dissolve away tin and the products retrieved. The materials were ground into fine powder for x-ray analysis which showed the diffraction patterns corresponding to the skutterudite structure.

The powders were then hot-pressed in graphite dies into dense samples, 2.0 mm long and 12.0 mm in diameter. The hot-pressing was conducted at a pressure of about 20,000 psi and at temperature of 1173 K for about 2 hours under argon atmosphere. Microprobe analysis (MPA) was performed on these samples to determine their atomic composition using a JEOL JXA-733 electron superprobe operating at  $20 \times 10^3$  Volts (V) of accelerating potential and  $25 \times 10^{-9}$  Amperes (A) of probe current. Pure elements and compounds were used as standards and x-ray intensity measurements of peak and background were conducted by wavelength dispersive spectrometry. The density of the samples was calculated from the measured weight and dimensions of the samples.

Samples in the form of disks (typically 1.0 mm thick and 12.0 mm diameter) were cut from the cylinders using a diamond saw (perpendicular to the pressing direction) for electrical and thermal transport property measurements. All samples were characterized at room temperature by Seebeck coefficient, Hall effect and electrical resistivity measurements. High temperature resistivity, Hall effect, Seebeck coefficient, thermal diffusivity, and heat capacity measurements were also conducted between room temperature and about 900K. The electrical resistivity ( $\rho$ ) was measured using the van der Paw technique with a current of 100 mA using a special high temperature apparatus<sup>29</sup>. The Hall coefficient ( $R_H$ ) was measured in the same apparatus with a constant magnetic field value of  $\sim 10,400$  Gauss. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by  $p = 1/R_{He}$ , where  $p$  is the density of holes, and  $e$  is the electron charge. The Hall mobility ( $\mu_H$ ) was calculated from the Hall coefficient and the resistivity values by  $\mu_H = R_H/\rho$ . Errors were estimated to be  $\pm 0.5\%$  and  $\pm 2\%$  for the resistivity and Hall coefficient data, respectively. The Seebeck coefficient ( $\alpha$ ) of the samples was measured on the same samples used for electrical resistivity and Hall coefficient measurements using a high temperature light pulse technique<sup>30</sup>.

The error of the Seebeck coefficient measurement was estimated to be less than  $\pm 3\%$ . The heat capacity and thermal diffusivity were measured using a flash diffusivity technique<sup>31</sup>. The thermal conductivity ( $\lambda$ ) was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall error in the thermal conductivity measurements was estimated to be about  $\pm 10\%$ . In addition, electrical resistivity and Seebeck coefficient measurements were conducted between 2K and 300K. A Quantum Design PPMS and indium contacts were used for resistivity measurements below room temperature. A Quantum Design PPMS utilizing Au-Fe 7% vs. chromel thermocouples and contacts was used for the low temperature thermopower measurements.

### III. RESULTS AND DISCUSSION

The room temperature properties of the  $\text{CoP}_3$  and  $\text{CeFe}_4\text{P}_{12}$  samples are listed in Table I. The measured lattice constants are in good agreement with literature values. Microprobe analyses showed that the  $\text{CoP}_3$  sample was single phase and its density was about 87% of theoretical density. Compared to their Sb-based analogs, phosphide skutterudite compounds require much higher temperature and pressure to achieve a density close to their theoretical values. The  $\text{CeFe}_4\text{P}_{12}$  sample was composed of 97% of a skutterudite phase having a composition  $\text{Ce}_{6.0}\text{Fe}_{21.9}\text{P}_{72.1}$ , while the remaining 3% was Ce and Fe based inclusions. The sample was 99% dense.

All samples had p-type conductivity at room temperature. The room temperature properties of  $\text{CoP}_3$  were typical of a semiconductor and consistent with the results obtained for  $\text{RhP}_3$  (see Table I). The Hall mobility was comparable to those obtained for  $\text{CoSb}_3$  at a similar doping level although the phosphide sample was not fully dense. This suggests that record high mobility values could be achieved provided that samples with higher density values can be prepared. The Seebeck coefficient of the binary  $\text{CoP}_3$  was lower than for its antimonide analog which suggests a very light hole effective mass. The room temperature properties of  $\text{CeFe}_4\text{P}_{12}$  were also indicative of a semiconductor, in agreement with previous findings<sup>26</sup> and calculations<sup>23</sup>. The room temperature Seebeck coefficient of the ternary phosphide compound was similar to those obtained for  $\text{CeFe}_4\text{Sb}_{12}$  although the carrier concentration of the sample was two orders of magnitude lower. This indicates again that the band masses of the antimonide are larger than those for the phosphide, in agreement with band structure calculations<sup>23</sup>.

The variations of the electrical resistivity and Seebeck coefficient as a function of temperature are shown in Figures 1 and 2, respectively. Typical values for  $\text{CeFe}_4\text{Sb}_{12}$  are also shown for comparison. The temperature dependence of the electrical resistivity for  $\text{CoP}_3$  is indicative of a semiconductor behavior at low temperatures. The weak temperature dependence at low temperatures suggests a small band gap which is consistent with an indirect band gap value of 0.07 eV calculated by Llunell et al.<sup>22</sup>. The onset of intrinsic conductivity is not observed even at the highest temperatures of measurements which is consistent with a relatively large pseudogap of about 1.26 eV calculated by Llunell et al. and also with the relatively high doping level of the sample. The Seebeck coefficient increases from room temperature to 800K while it becomes n-type below 250K where electrons dominate the conduction. For  $\text{CeFe}_4\text{P}_{12}$  the temperature dependence of the resistivity indicates a semiconductor behavior which clearly contrasts with  $\text{CeFe}_4\text{Sb}_{12}$  for which the resistivity increases with increasing temperature. Above 150K, intrinsic conduction is observed and the resistivity decreases linearly with increasing temperature. An activated energy of 0.25 eV was calculated between 300 and 450K which is to be compared to a calculated band gap of 0.34 eV<sup>23</sup>.

We now turn our discussion to the thermal conductivity data which are shown in Figure 3. The data shown correspond to the total thermal conductivity. The thermal conductivity is strongly influenced by the density of the sample measured. Although the data shown in Figure 3 correspond to nearly fully dense  $\text{CeFe}_4\text{Sb}_{12}$ ,  $\text{CeFe}_4\text{P}_{12}$ , and  $\text{CoSb}_3$  samples, the density of the

CoP<sub>3</sub> sample is only about 87% (see Table I). The thermal conductivity values of a fully dense material are expected to be somewhat larger than the values measured on our sample. The room temperature thermal conductivity is about 185 mW/cmK which is to be compared to 100 mW/cmK for CoSb<sub>3</sub> and 145 mW/cmK for CoAs<sub>3</sub>.<sup>32</sup> There seems therefore that the thermal conductivity increases in the Co binary skutterudite compounds series going from the antimonide to the phosphide. This result is consistent with the fact that compounds formed with heavier elements tend to possess lower lattice thermal conductivity. The temperature dependence of the thermal conductivity for the CoP<sub>3</sub> sample is similar to the results obtained for CoSb<sub>3</sub><sup>16</sup> and follows a 1/T dependence which suggests a predominant phonon-phonon umklapp scattering above room temperature. The thermal conductivity reaches a minimum about 120 mW/cmK at 750K and then increases slightly due to minority carriers contributing to the conduction.

Slack and Tsoukala<sup>13</sup> first pointed out that the skutterudite structure have large voids which can be filled by rare-earth atoms and that this filling can be used to reduce the lattice thermal conductivity of these materials. The rare-earth atom would rattle inside the void and interact with the lattice vibrations. This has now been experimentally confirmed on a number of filled skutterudite compounds including CeFe<sub>4</sub>Sb<sub>12</sub>.<sup>2,18</sup> Typical thermal conductivity data for CeFe<sub>4</sub>Sb<sub>12</sub><sup>2</sup> are also shown in Figure 3. The thermal conductivity for CeFe<sub>4</sub>Sb<sub>12</sub> shows only a weak temperature dependence and the values are significantly smaller than those obtained for binary compounds. These low values have been predominantly attributed to the “rattling” of the Ce ions<sup>18</sup>. By contrast, the thermal conductivity for CeFe<sub>4</sub>P<sub>12</sub> is relatively large and shows a 1/T temperature dependence. At room temperature, the thermal conductivity value is 145 mW/cmK, larger than the value for undoped CoSb<sub>3</sub> (100 mW/cmK). There are two factors contributing to this somewhat surprising result. First, it seems that Ce ions do not produce a similar phonon scattering as the one observed in CeFe<sub>4</sub>Sb<sub>12</sub>. The lattice constant for CeFe<sub>4</sub>Sb<sub>12</sub> is 9.1350 Å while the cell is much smaller for CeFe<sub>4</sub>P<sub>12</sub> (a = 7.7920 Å). The Ce ions are therefore not as free to “rattle” inside the empty cages of CeFe<sub>4</sub>P<sub>12</sub> and they do not decrease the thermal conductivity. This result demonstrates that the thermal vibration amplitude of the rare earth atom strongly depends on its size relative to the volume of the cage. Second, the hole concentration is two orders of magnitude lower in the ternary phosphide compared to the antimonide. While phonons are substantially scattered by holes in heavily doped skutterudites materials such as CeFe<sub>4</sub>Sb<sub>12</sub> and n-type CoSb<sub>3</sub><sup>16</sup>, this type of scattering is substantially lower than in the phosphide with a lower hole density. It seems therefore that both a reduced motion of the Ce ions and lower hole-phonon scattering are responsible for the relatively large thermal conductivity of CeFe<sub>4</sub>P<sub>12</sub>.

One can calculate the rattling amplitude which is defined as the difference between the void filler covalent radius to the radius of the cage. The rattling amplitude has been calculated for some filled skutterudite materials and the values are listed in Table II. One can see that the rattling amplitude increases going from the phosphides to the antimonides which have larger unit cell and cage size. For Ce-filled materials, the rattling amplitude increases from Fe-based to Ru based materials which is also a consequence of slightly larger unit cells and cage sizes. From the same table, the impact of the cage size on the lattice thermal conductivity is dramatic and the larger the rattling amplitude is, the lower the thermal conductivity is. Another measure of the effectiveness of the void filler in scattering phonons is the thermal parameter which is a measure of the ability of the rare-earth ion to “rattle” inside the cage. The thermal parameters values are also listed in Table II. The larger values are obtained for the antimonide compounds and the values for the arsenide and phosphide are substantially lower. Our results correlate these trends and support the idea that the choice of the rattling atom is crucial when trying to lower the lattice thermal conductivity of these materials. One should however bear in mind the effects of charge carrier scattering which can significantly contribute to the decrease in lattice thermal conductivity of skutterudite materials.

The calculated ZT values for CoP<sub>3</sub> and CeFe<sub>4</sub>P<sub>12</sub> are relatively low with a maximum at 800K of 0.01 and 0.08, respectively. These low values compared to their antimonide analogs seem to be

primarily due to their larger thermal conductivity. They however show semiconducting behavior and their thermoelectric properties may therefore be more tunable than the antimonides. Significant reduction in lattice thermal conductivity in skutterudite materials can be obtained when phonons are scattered by charge carriers<sup>16</sup>, electrons transferred between mixed valence atoms<sup>33</sup>, void fillers and point defects. These mechanisms do not scatter phonons in the same frequency range and if one wants to obtain the lattice thermal conductivity close to the theoretical minimum value, it is necessary to scatter phonons in the whole frequency spectrum. It seems therefore that solid solutions between filled antimonides and phosphides are prime candidates for further studies and optimization of the thermoelectric properties of these materials. In such solid solutions, the lattice thermal conductivity could be reduced by both void filling and mass and volume fluctuation on the anion sites. In addition, these compositions are expected to be semiconducting. Other binary and ternary phosphide compounds are currently being synthesized to confirm the trends described in this paper and further establish strategies for optimizing the thermoelectric properties of this interesting class of compounds.

#### IV. CONCLUSION

CoP<sub>3</sub> and CeFe<sub>4</sub>P<sub>12</sub> samples have been synthesized and their thermoelectric properties have been measured for the first time. Both compounds have p-type conduction and show semiconducting behavior. CoP<sub>3</sub> is characterized by large hole mobility values, relatively small Seebeck coefficient and large thermal conductivity. The thermal conductivity of CeFe<sub>4</sub>P<sub>12</sub> is about ten times larger than for CeFe<sub>4</sub>Sb<sub>12</sub> which is primarily due to both a reduced motion of the Ce ions in smaller voids and lower hole-phonon scattering. These findings have helped establish a trend for the optimization of this class of materials. In particular, they point to criteria for selecting the most promising semiconducting compositions which combine both point defects and void filling scattering. Such compositions are currently being synthesized and their properties measured.

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Table I. Some room temperature properties of CoP<sub>3</sub> and CeFe<sub>4</sub>Sb<sub>12</sub> and other skutterudite compounds

	Units	CoP <sub>3</sub>	CoSb <sub>3</sub> <sup>a</sup>	RhP <sub>3</sub> <sup>b</sup>	CeFe <sub>4</sub> P <sub>12</sub>	CeFe <sub>4</sub> Sb <sub>12</sub> <sup>c</sup>
Lattice constant	(Å)	7.7073	9.0345	7.9951	7.7917	9.1350
Percentage of the theoretical density	%	87	99.9	99.6	99	99
Type of conductivity		p	p	p	p	p
Electrical resistivity	mΩcm	0.26	0.44	1.4	20.5	0.75
Seebeck coefficient	μV/K	15	108	32	58	59
Hall carrier concentration	10 <sup>19</sup> /cm <sup>3</sup>	3.26	1	6	1.42	550
Hall mobility	cm <sup>2</sup> /Vs	748	1432	745	24.9	1.5
Thermal conductivity	mW/cmK	185	100	-	140	14

<sup>a</sup>Reference 16.

<sup>b</sup>Reference 28.

<sup>c</sup>Reference 2 and 10.

Table II. Some properties of several filled skutterudite compositions at 300K from literature. Data in italic were extrapolated.

	Lattice parameter (Å)	Cage radius (Å)	Rare-earth covalent radius (Å)	Rattling amplitude (Å)	Thermal parameter (Å <sup>2</sup> )	Lattice thermal conductivity (mW/cmK)
LaFe <sub>4</sub> P <sub>12</sub>	7.832	1.806	1.69	0.116	0.4	-
LaFe <sub>4</sub> As <sub>12</sub>	8.325	1.861	1.69	0.171	0.61	-
LaFe <sub>4</sub> Sb <sub>12</sub>	9.140	1.933	1.69	0.243	1.3	17
CeFe <sub>4</sub> P <sub>12</sub>	7.792	1.800	1.65	0.150	0.42	140
CeFe <sub>4</sub> As <sub>12</sub>	8.296	<i>1.852</i>	1.65	0.202	<i>0.86</i>	-
CeFe <sub>4</sub> Sb <sub>12</sub>	9.145	<i>1.936</i>	1.65	0.286	<i>1.90</i>	14
CeRu <sub>4</sub> P <sub>12</sub>	8.038	<i>1.827</i>	1.65	0.177	<i>0.68</i>	86 <sup>a</sup>
CeRu <sub>4</sub> As <sub>12</sub>	8.491	<i>1.871</i>	1.65	0.221	<i>1.03</i>	-
CeRu <sub>4</sub> Sb <sub>12</sub>	9.266	<i>1.948</i>	1.65	0.298	<i>2.13</i>	-

<sup>a</sup>Reference 34.

### Figure Captions

Figure 1. Electrical resistivity of CoP<sub>3</sub>, CeFe<sub>4</sub>P<sub>12</sub> and CeFe<sub>4</sub>Sb<sub>12</sub><sup>a</sup> as a function of temperature .  
(<sup>a</sup> Reference 2.)

Figure 2. Seebeck coefficient of CoP<sub>3</sub>, CeFe<sub>4</sub>P<sub>12</sub> and CeFe<sub>4</sub>Sb<sub>12</sub><sup>a</sup> as a function of temperature. (<sup>a</sup> Reference 2.)

Figure 3. Thermal conductivity of CoP<sub>3</sub>, CoSb<sub>3</sub><sup>a</sup>, CeFe<sub>4</sub>P<sub>12</sub> and CeFe<sub>4</sub>Sb<sub>12</sub><sup>b</sup> as a function of temperature. (<sup>a</sup> Reference 16., <sup>b</sup> Reference 2.)







